Understanding Ammonia Oxidation on Transition Metals

Third Annual ECS Guelph Young Researcher Symposium

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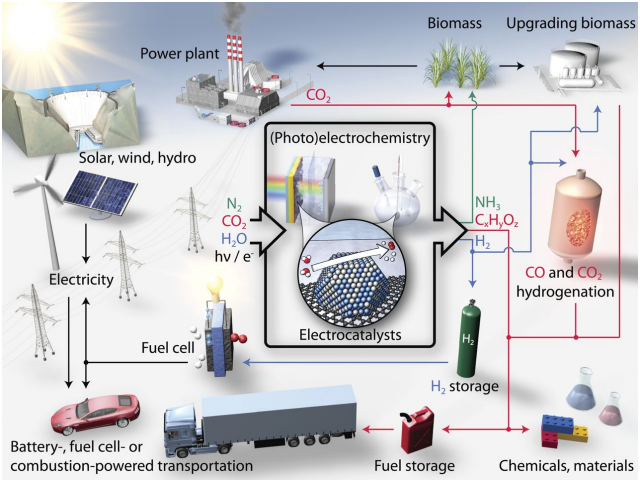
University of Guelph

UNIVERSITY OF GUELPH

College of Computational, Mathematical, and Physical Sciences

Electrochemical Technology Centre

The Energy Transformation Challenge



Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Jaramillo, T. F. *Science* **2017**, *355*, eaad4998.

mechanistic understanding

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stable, active, and selective electrocatalysts

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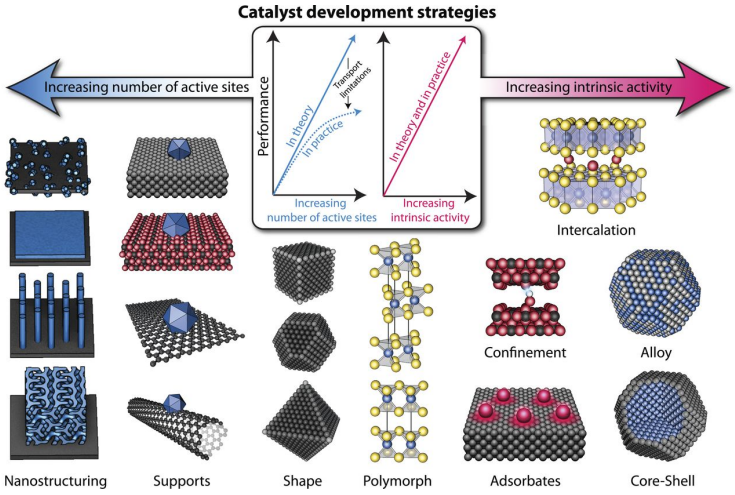
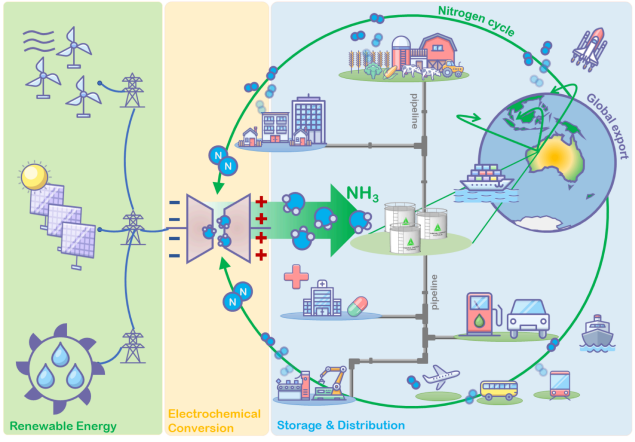
Strategies to Improve Electrocatalysts



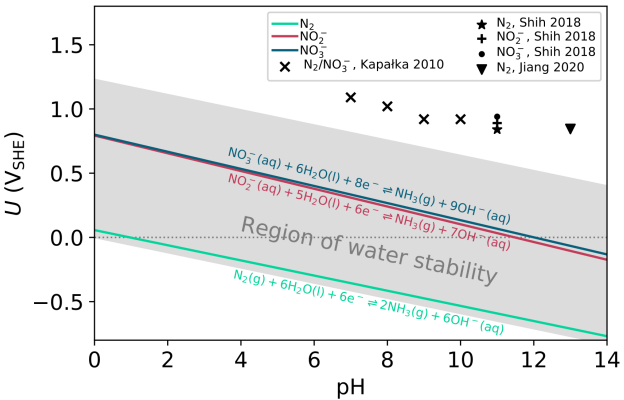
Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Jaramillo, T. F. *Science* **2017**, *355*, eaad4998.

The Ammonia Economy



MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; Simonov, A. N. *Joule* **2020**, *17*, 1186–1205.

Ammonia Oxidation Pourbaix Diagram



Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, e2100142.

The Computational Hydrogen Electrode (CHE)

Our reference is the half-reaction

$$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g) \tag{1}$$

This reaction is defined to be at equilibrium at $U = 0$ V, pH $= 0$, and $p_{H_2} = 101325$ Pa. Then we can equate the chemical potentials of the proton-electron pair with half that of the gas-phase H_2 molecule

$$\mu_{H^+(aq)} + \mu_{e^-} = \frac{1}{2}\mu_{H_2(g)} \tag{2}$$

Additional terms are added to include the effects of pH and potential shifts

$$\mu_{H^+(aq)}([H^+]) + \mu_{e^-}(U) = \frac{1}{2}\mu_{H_2(g)} + RT \ln \left(\frac{\sqrt{p_{H_2}}}{[H^+]} \right) - eU \tag{3}$$

Nørskov, J.K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.

Applying the CHE in Alkaline Conditions

$$H_2O(l) + e^- \rightleftharpoons \frac{1}{2} H_2(g) + OH^-(aq), \quad U^{\ominus} = -0.83 \text{ V versus SHE, pH = 14} \tag{4}$$

$$\mu_{OH^-(aq)} - \mu_{e^-} = \mu_{H_2O(l)} - \frac{1}{2}\mu_{H_2(g)} + RT \ln \left(\frac{\sqrt{p_{H_2}} \left[OH^-\right]}{a_{H_2O(l)}} \right) - (0.83 + eU) \tag{5}$$

To calculate the energy change of an adsorption step

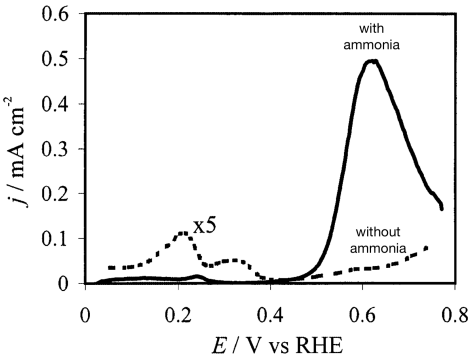
$$Al + OH^-(aq) \rightarrow AlOH* + e^- \tag{6}$$

We have

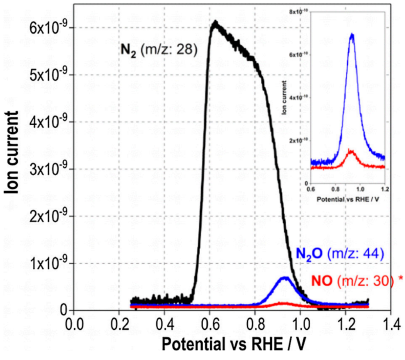
$$\Delta G = G_{AlOH*} - G_{Al} - \left[\mu_{H_2O(l)} - \frac{1}{2}\mu_{H_2(g)} + RT \ln \left(\frac{\sqrt{p_{H_2}} \left[OH^-\right]}{a_{H_2O(l)}} \right) - (0.83 + eU) \right] \tag{7}$$

Chen, L. D.; Nørskov, J. K.; Luntz, A. C. *J. Phys. Chem. Lett.* **2014**, *119*, 19660–19667.

Ammonia Oxidation on Pt

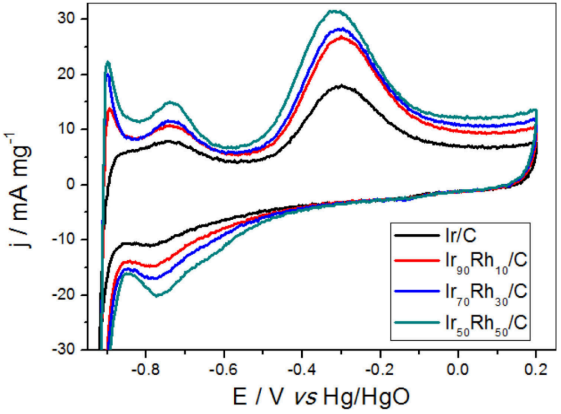


de Vooys, A. C. A.; Koper, M. T. M.; van Santen, R. A.; van Veen, J. A. R. *Electroanal. Chem.* **2001**, *506*, 127–137.



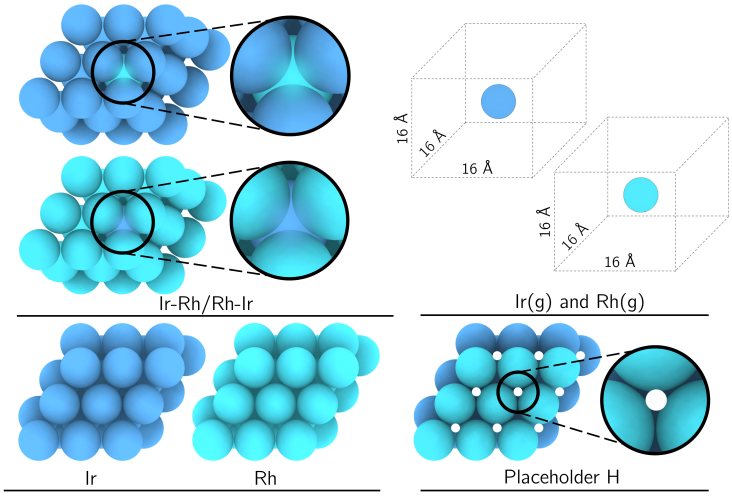
Katsounaros, I.; Figueiredo, M. C.; Calle-Vallejo, F.; Li, H.; Gewirth, A. A.; Marković, N. M.; Koper, M. T. M. *J. Catal.* **2018**, *359*, 82–91.

Ammonia Oxidation on Ir-Rh Alloys



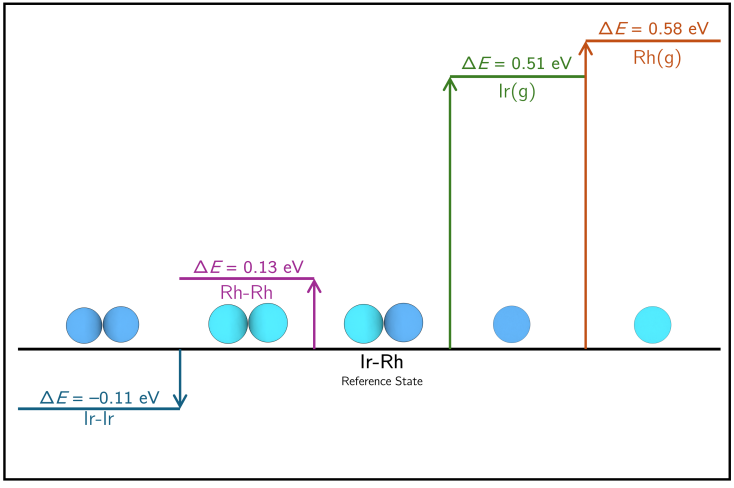
Silva, J. C. M.; Assumpção, M. H. M. T.; Hammer, P.; Neto, A. O.; Spinacé, E. V.; Baranova, E. A. *ChemElectroChem* **2017**, *17*, 1101–1107.

Quantifying Ir-Rh Interactions



Laframboise, B. J. R.; Johnston, S. J.; Chen, L. D. *ChemCatChem* **2025**, *17*, e202401177.

Quantifying Ir-Rh Interactions



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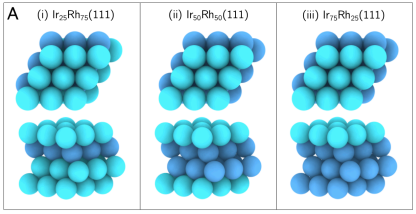
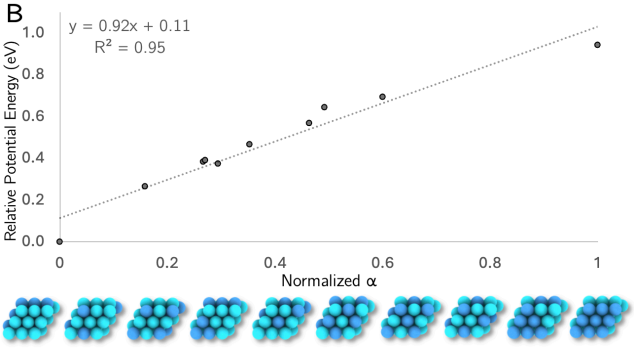
Quantifying Ir-Rh Interactions





$$\alpha = \sum_{i=1}^{N} \sum_{j=1}^{12} E_{ij} \qquad (8)$$

$$\text{Normalized } \alpha_n = \frac{\alpha_n - \text{Min}(\alpha)}{\text{Max}(\alpha) - \text{Min}(\alpha)} \qquad (9)$$

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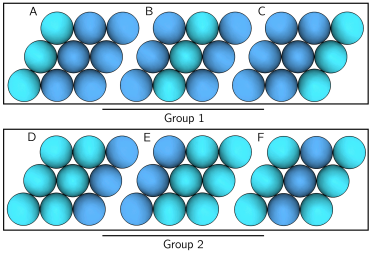
Accounting for Configurational Entropy



$$n_1 = n_2 = n_{\text{elements}}^{r} = 3^2 = 9 \tag{10}$$

$$n_{\text{layers}} = \binom{4}{2} = 6 \tag{11}$$

$$n_{\text{total}} = n_1 \cdot n_2 \cdot n_{\text{layers}} = 9 \cdot 9 \cdot 6 = 486 \tag{12}$$

Group 1 Layers	Group 2 Layers	Layer Ordering
9 states	**9 states**	**6 states**
A,A	D,D	G1,G1,G2,G2
B,A	E,D	G1,G2,G1,G2
C,A	F,D	G2,G1,G2,G1
A,B	D,E	G2,G2,G1,G1
A,C	D,F	G1,G2,G2,G1
B,B	E,E	G2,G1,G1,G2
B,C	E,F	
C,B	F,E	
C,C	F,F	

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Accounting for Configurational Entropy

Group	Ir Count	Rh Count	Number of States
G_0	0	9	1
G_1	1	8	9
G_2	2	7	36
G_3	3	6	84
G_4	4	5	126
G_5	5	4	126
G_6	6	3	84
G_7	7	2	36
G_8	8	1	9
G_9	9	0	1

To maintain the 1:1 ratio of Ir and Rh, only combinations of layers with indices that sum up to 18 are considered. For example, the combination $[G_4, G_1, G_6, G_7]$ is valid, however, the combination $[G_8, G_5, G_3, G_9]$ is not.

$$n_i = \binom{9}{n_{\mathrm{Ir}}} \tag{13}$$

$$n_{\mathrm{total}} = \prod_{i=1}^{4} n_{\mathrm{i}} \tag{14}$$

Using Python, it was found that there are 670 valid combinations for a 1:1 ratio of Ir and Rh. Then, taking into account the number of possible states for each group, we end up with a total of 9,075,135,300 configurations, which is equal to $\binom{36}{18}$.

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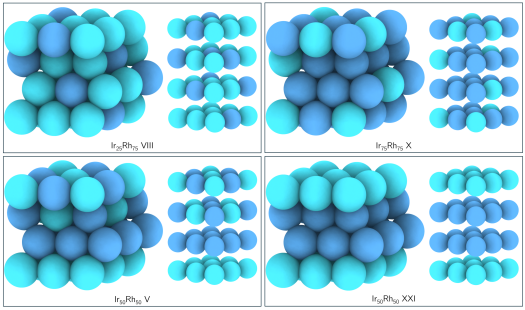
Accounting for Configurational Entropy



$$S = k_B \ln \Omega \qquad (15)$$

Alloy Index	Number of States	$-TS_{\text{config}}$ (eV)
I	1	0
IV	1	0
II	7056	−0.228
III	7056	−0.228
V	15876	−0.248
VI	15876	−0.248
VII	381024	−0.330
X	2286144	−0.376
VIII	2286144	−0.376
IX	3919104	−0.390

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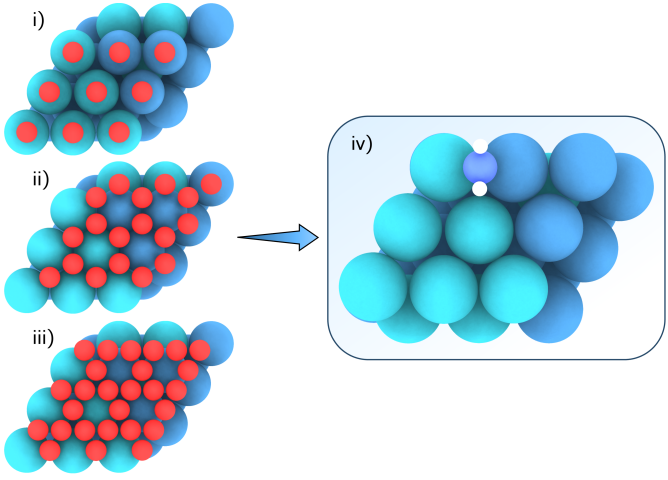
Site Testing on Alloy Surfaces



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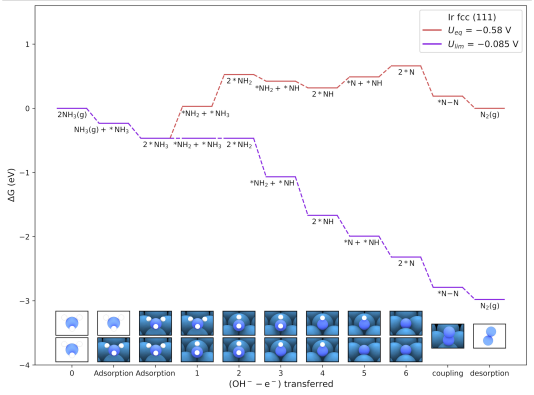
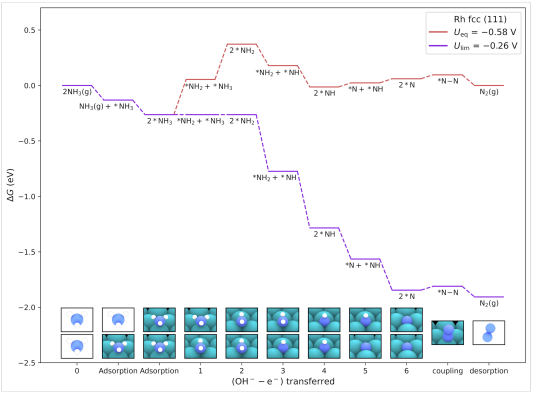
N_2 Formation on Pure Ir and Rh





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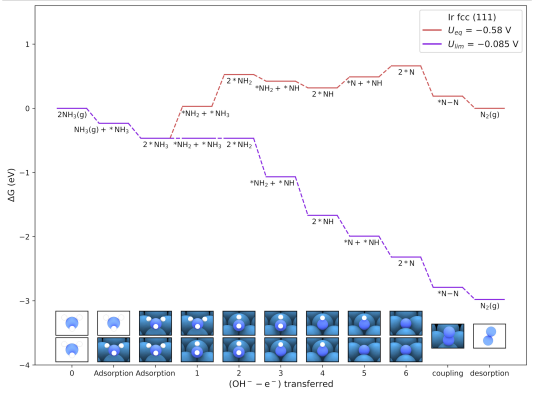
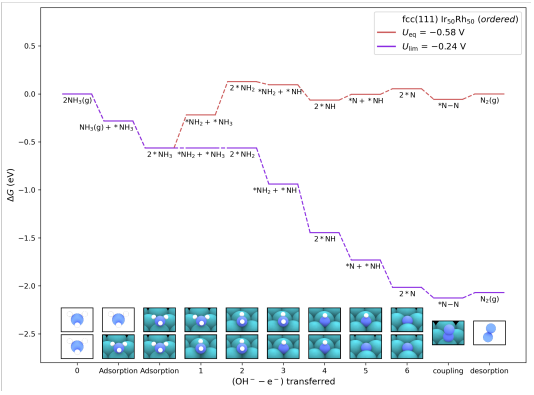
N_2 Formation Is Favoured on 50:50 Ir-Rh Alloy





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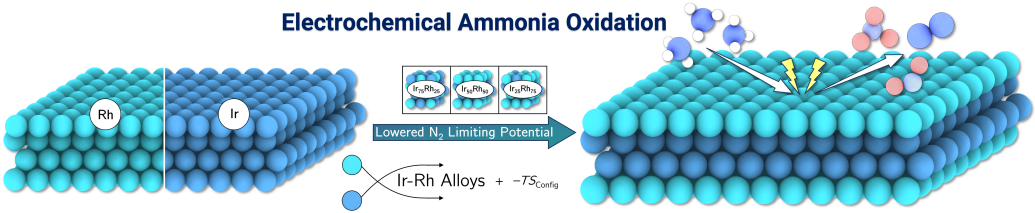
Ir-Rh Alloy Summary



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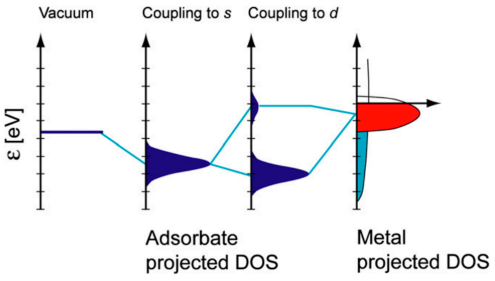
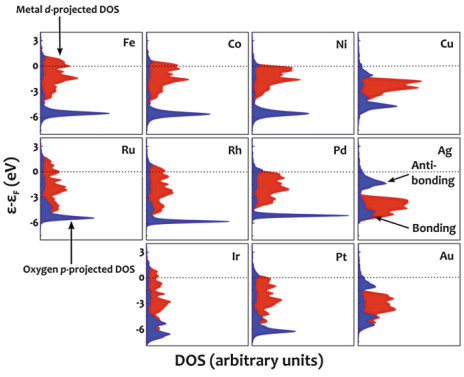
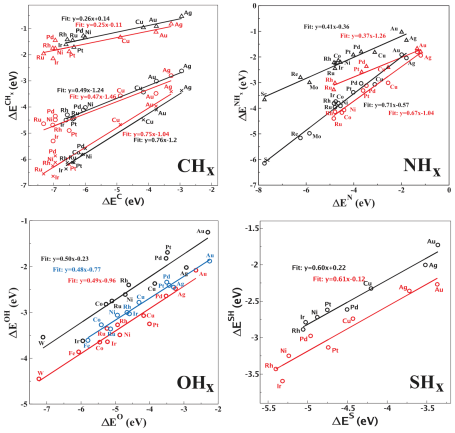
The *d*-band Model





Nørskov, J. K.; Studt, F.; Abild-Pedersen, F.; Bligaard, T. *Fundamental Concepts in Heterogeneous Catalysis*; John Wiley & Sons, 2014.

Scaling Relations

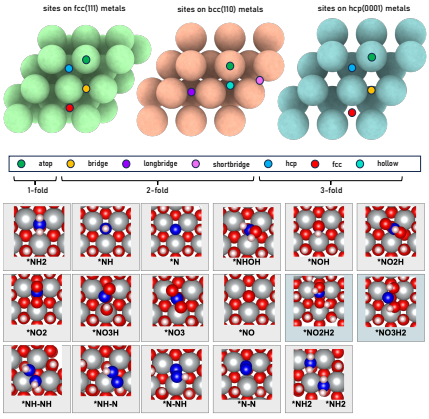


Abild-Pedersen, F.; Greeley, J.; Studt, F.; Rossmeisl, J.; Munter, T. R.; Moses, P. G.; Skúlason, E.; Bligaard, T.; Nørskov, J. K. *Phys. Rev. Lett.*; **2007**, *99*, 016105.

Calculation Details

: reference metals : test metals : excluded species

3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	1 IB	1 IIB
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn



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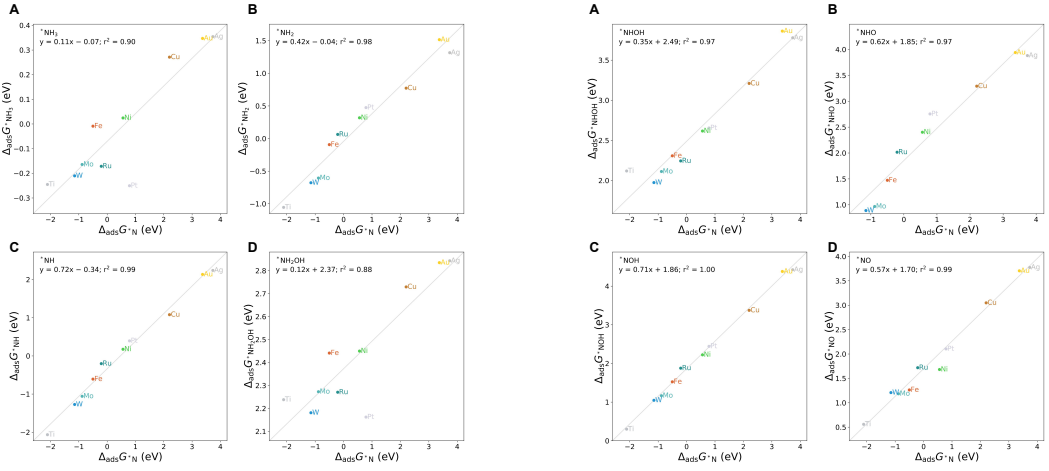
Scaling Relations for Ammonia Oxidation Intermediates



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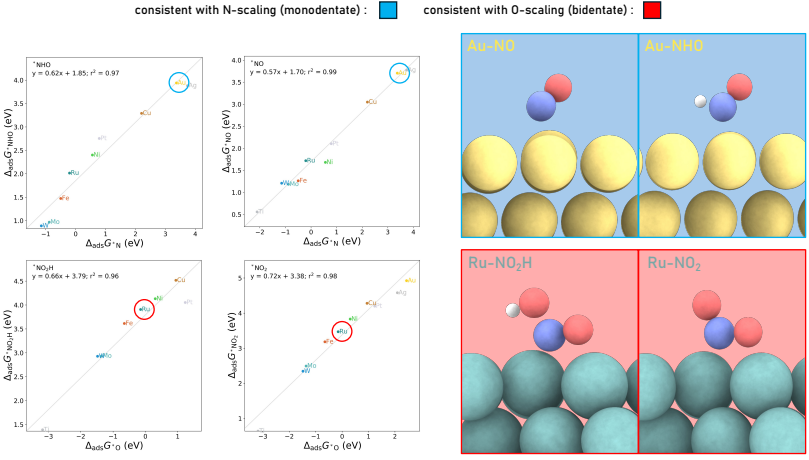
Monodentate and Bidentate Adsorbates



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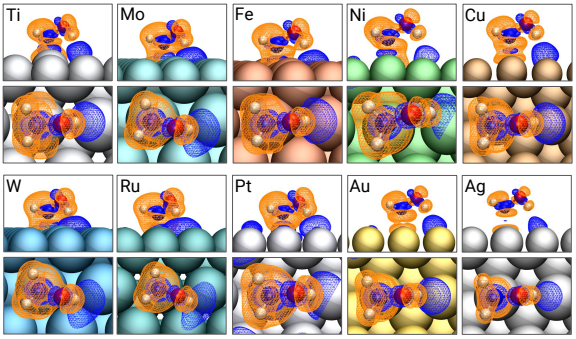
Adsorbate-Surface Hydrogen Bonding



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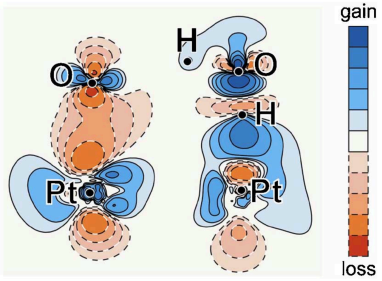
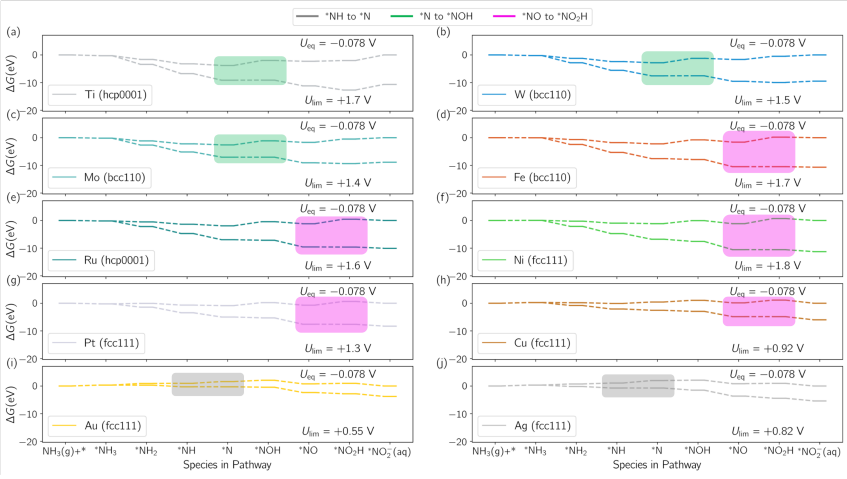


Ogasawara, H.; Brena, B.; Nordlund, D.; Nyberg, M.; Pelmenschikov, A.; Pettersson, L. G. M.; Nilsson, A. *Phys. Rev. Lett.* **2002**, *89*, 276102.

Microkinetic Modelling



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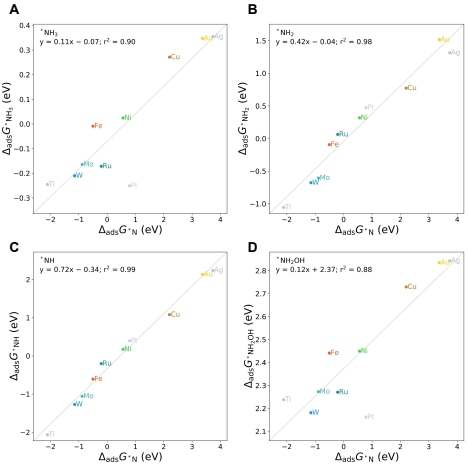
Microkinetic Modelling



$$^{*}NH_2 + OH^{-}(aq) \rightarrow {}^{*}NH + H2O\,(l) + e^{-}$$

$$\Delta_r G\,(\mathrm{pH},\, U) = (m_{*\mathrm{NH}} - m_{*\mathrm{NH_2}})\Delta_{\mathrm{ads}} G_{*\mathrm{N}} + (b_{*\mathrm{NH}} - b_{*\mathrm{NH_2}}) + 0.5 G_{\mathrm{H_2(g)}} - eU - 0.65\,\mathrm{eV}$$

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Microkinetic Modelling

$$\mathrm{NH_3(g)} + * \rightarrow {}^*\mathrm{NH_3} \tag{16}$$

$${}^*\mathrm{NH_3} + \mathrm{OH^-(aq)} \rightarrow {}^*\mathrm{NH_2} + \mathrm{H_2O(l)} + \mathrm{e^-} \tag{17}$$

$${}^*\mathrm{NH_2} + \mathrm{OH^-(aq)} \rightarrow {}^*\mathrm{NH} + \mathrm{H_2O(l)} + \mathrm{e^-} \tag{18}$$

$${}^*\mathrm{NH} + \mathrm{OH^-(aq)} \rightarrow {}^*\mathrm{N} + \mathrm{H_2O(l)} + \mathrm{e^-} \tag{19}$$

$${}^*\mathrm{N} + \mathrm{OH^-(aq)} \rightarrow {}^*\mathrm{NOH} + \mathrm{e^-} \tag{20}$$

$${}^*\mathrm{NOH} + \mathrm{OH^-(aq)} \rightarrow {}^*\mathrm{NO} + \mathrm{H_2O(l)} + \mathrm{e^-} \tag{21}$$

$${}^*\mathrm{NO} + \mathrm{OH^-(aq)} \rightarrow {}^*\mathrm{NO_2H} + \mathrm{e^-} \tag{22}$$

$${}^*\mathrm{NO_2H} \rightarrow \mathrm{NO_2H(g)} + * \tag{23}$$

$$r = \frac{k_\mathrm{B}T}{h} e^{\frac{-E_\mathrm{a}(\mathrm{RDS})}{k_\mathrm{B}T}} [\mathrm{NH_3}][\mathrm{OH^-}]^4 K_1 K_2 K_3 K_4 \theta_* \left(1 - \gamma_\mathrm{eq}\right) \tag{24}$$

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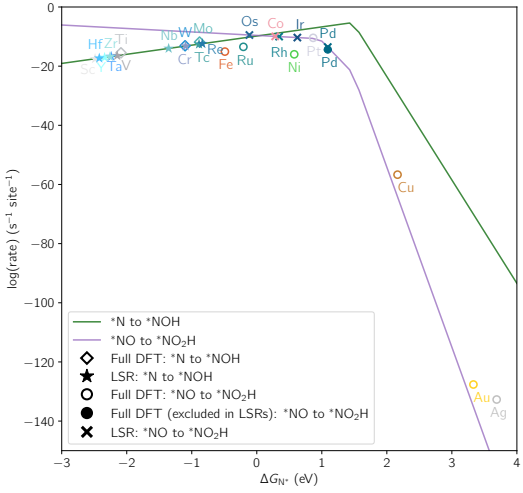
Microkinetic Modelling



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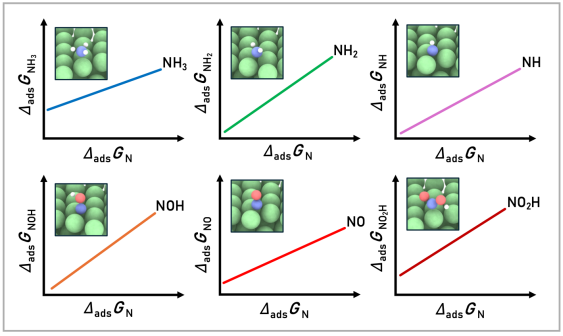
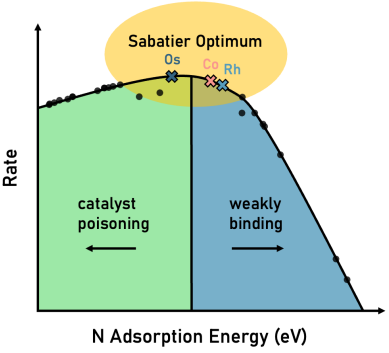
Ammonia Oxidation Scaling Relations Summary

Linear Scaling Relations for NO_xH_y



AOR Sabatier Plot for NO_2^- Formation



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Dr. J. Zhou*
LOHCs **(13:15)**

B. Laframboise
Pt Alloys **(16:01)**

B. Paget
Ni Oxide **(16:22)**

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